

(19)



Eur päisch s Pat ntamt

Eur pean Patent Office

Offi e uropéen des brevets



(11)

EP 0 870 819 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
14.10.1998 Bulletin 1998/42

(51) Int Cl.⁶: **C10L 1/22, C10L 1/14,
C10L 10/00**

(21) Application number: **98302812.7**

(22) Date of filing: **09.04.1998**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **10.04.1997 US 837246**

(71) Applicant: **ETHYL CORPORATION**
Richmond, Virginia 23219-4304 (US)

(72) Inventors:
• **Malfer, Dennis J.**
Glen Allen, Virginia 23060 (US)
• **Franklin, Randall M.**
Mechanicsville, Virginia 23116 (US)
• **Colucci, William L.**
Glen Allen, Virginia 23060 (US)

(74) Representative: **Smaggasgale, Gillian Helen et al**
Mathys & Squire,
100 Gray's Inn Road
London WC1X 8AL (GB)

(54) **Additives for minimizing intake valve deposits, and their use**

(57) New, highly effective detergent/dispersants for use in spark ignition fuels are described. They are Mannich condensation products formed from (i) one mole part of at least one substituted hydroxyaromatic compound having on the ring both (a) an aliphatic hydrocarbyl substituent derived from a polyolefin having a number average molecular weight in the range of about 500 to about 3000, and (b) a C₁₋₄ alkyl; (ii) from 0.8 to 1.5 mole part(s) of aliphatic polyamine having one and

only one primary or secondary amino group in the molecule capable of participating in the Mannich condensation reaction; and (iii) from 0.8 to 1.3 mole part(s) of aldehyde, provided that the mole ratio of aldehyde to amine is 1.2:1 or less. Carrier fluids such as poly(oxyalkylene) compounds further enhance the effectiveness of these Mannich condensation products in minimizing or reducing intake valve deposits and/or intake valve sticking.

EP 0 870 819 A2

Description

TECHNICAL FIELD

5 This invention relates to novel Mannich base fuel additive compositions that are effective in minimizing intake valve deposits and in reducing valve sticking in internal combustion engines.

BACKGROUND

10 Despite extensive prior research activities on Mannich base fuel additives carried out over the years, a need exists for Mannich base compositions having superior performance capabilities and superior physical properties. In particular, a most welcome contribution to the art would be the provision of Mannich base compositions that are highly effective in minimizing intake valve deposits in internal combustion engines, that are capable of minimizing valve sticking under standard qualification test conditions, that have much less color than present commercial Mannich fuel detergents, 15 that have minimal odor, that require, and in many cases perform better with, smaller amounts of liquid carrier fluids than are conventionally used, and that provide all of these advantages at attractive competitive costs.

This invention is deemed to constitute such a contribution.

SUMMARY OF THE INVENTION

20 This invention is based, inter alia, on the discovery that Mannich condensation products having superior performance characteristics and excellent physical properties can be formed by using certain types of polyamines in the condensation reaction and by using the reactants, which include these particular polyamines, in special proportions relative to each other. Further, it has been discovered that by using a disubstituted phenol which has only one site for the 25 Mannich reaction to occur, i.e., only one ortho- or para- position being unsubstituted, products are obtained which are more effective at reducing intake valve deposits on an active/active basis compared to Mannich base products derived from a hydroxyaromatic compound having two or three reactive sites. The term "active" means the total mass of amine-containing products, regardless of chemical identity, thus compounds of the present invention are more effective at reducing intake valve deposits than compounds derived from a hydroxyaromatic compound substituted in only one 30 position when both Mannich products contain equivalent amounts of amine-containing products. Also, the improved Mannich base products of the present invention can be made in higher yields compared to products made from a hydroxyaromatic compound substituted in only one position.

Thus, in one of its embodiments this invention provides a Mannich product formed from a mixture of (i) one mole part of at least one substituted hydroxyaromatic compound having on the ring both (a) an aliphatic hydrocarbyl sub- 35 stituent derived from a polyolefin having a number average molecular weight in the range of about 500 to about 3000, and (b) a C_{1-4} alkyl; (ii) from 0.8 to 1.3 mole part(s) of at least one aldehyde; and (iii) from 0.8 to 1.5 mole part(s) of at least one aliphatic polyamine having in the molecule one primary or secondary amino group capable of undergoing a Mannich condensation reaction with (i) and (ii), the other amino group or groups in the molecule being substantially inert toward direct participation in such Mannich condensation reaction, with the proviso that the mole ratio of aldehyde 40 to amine is 1.2:1 or less. Preferred products of this type are formed by heating a mixture formed from (i), (ii) and (iii), at a temperature above about 40°C at which a Mannich condensation reaction takes place. Preferred aliphatic polyamines have in the molecule one and only one such reactive primary or secondary amino group and one or more tertiary amino groups.

Another embodiment of this invention is a fuel additive composition which comprises:

- 45
- A) a Mannich product as described above, and
 - B) at least one liquid carrier or induction aid therefor, most preferably at least one poly(oxyalkylene) compound having an average molecular weight in the range of about 500 to about 3000.

50 Still another embodiment is the above-described process by which the above improved Mannich product of this invention is produced.

Other embodiments include fuels for spark ignition engines into which have been blended small amounts of the various compositions of this invention described herein, and methods for minimizing or reducing intake valve deposits and/or minimizing or reducing intake valve sticking in an internal combustion engine by fueling and/or operating th 55 engine with a fuel composition of this invention.

In additional preferred embodiments of this invention the Mannich product is formed from one mole part of a substituted phenol in which the hydrocarbyl substituent (a) comprises polypropylene, polybutylene or a copolymer of propylene and butylene having a number average molecular weight in the range of about 500 to about 3000 and a poly-

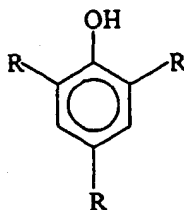
dispersity in the range of about 1 to about 4, from 0.8 to 1.2 mole part(s) of one or more N,N-dialkyl- α,ω -alkylene-diamines in which the alkylene group has at least 3 carbon atoms, and from 0.8 to 1.2 mole parts of formaldehyde, provided the molar ratio of formaldehyde to the diamine(s) is 1.2:1 or less. Because of outstanding effectiveness in control (i.e., reduction or minimization) of the weight of deposits formed on intake valves during engine operation, an especially preferred embodiment involves use of N,N-dimethyl-1,3-propanediamine as the polyamine, formaldehyde as the aldehyde, and a molar ratio of the above substituted phenol to N,N-dimethyl-1,3-propanediamine to formaldehyde of 1:1-1.15:0.90-1.20, respectively, with the proviso that if the molar quantity of formaldehyde is larger than the molar quantity of the amine, the excess molar amount of the formaldehyde does not exceed about 0.1. The most preferred molar ratio for these last-named reactants is about 1 mole of the N,N-dimethyl-1,3-propanediamine and about 1.05 mole of formaldehyde per mole of the above substituted phenol. Such Mannich base reaction products have given superlative results in an extensive number of tests.

Other embodiments and features of this invention will become still further apparent from the ensuing description and appended claims.

FURTHER DETAILED DESCRIPTION

Mannich Base Reaction Product

Representative high molecular weight substituted hydroxyaromatic compounds used in forming the present Mannich base products are represented by the following formula:



in which R is H, C_{1-4} alkyl, or a hydrocarbyl substituent having a number average molecular weight in the range of about 500 to about 3000, with the proviso that one R is H, one R is a C_{1-4} alkyl and one R is a hydrocarbyl substituent. It has been discovered that by using a substituted phenol which has only one site for the Mannich reaction to occur, i.e., only one ortho- or para-position being unsubstituted, products are obtained which are more effective at reducing intake valve deposits on an active/active basis compared to Mannich base products derived from a hydroxyaromatic compound having two or three reactive sites. Further, the Mannich base products of the present invention can be made in higher yields compared to products made from a hydroxyaromatic compound substituted in only one position.

Representative hydrocarbyl substituents include polypropylene, polybutene, polyisobutylene, and copolymers of butylene and propylene. Other similar long-chain hydrocarbyl substituents may be used, but are less preferred. Examples include copolymers of butylene and/or isobutylene and/or propylene, and one or more mono-olefinic comonomers copolymerizable therewith (e.g., ethylene, 1-pentene, 1-hexene, 1-octene, 1-decene, etc.) where the copolymer molecule contains at least 50 % by weight, of butylene and/or isobutylene and/or propylene units. The comonomers polymerized with propylene or such butenes may be aliphatic and can also contain non-aliphatic groups, e.g., styrene, o-methylstyrene, p-methylstyrene, divinyl benzene and the like. Thus in any case the resulting polymers and copolymers used in forming the substituted phenolic reactant are substantially aliphatic hydrocarbon polymers. Polybutylene is preferred. Unless otherwise specified herein, the term "polybutylene" is used in a generic sense to include polymers made from "pure" or "substantially pure" 1-butene or isobutene, and polymers made from mixtures of two or all three of 1-butene, 2-butene and isobutene. Commercial grades of such polymers may also contain insignificant amounts of other olefins. So-called high reactivity polybutylenes having relatively high proportions of polymer molecules having a terminal vinylidene group, i.e. at least 20% of the total olefin comprises an alkylvinylidene isomer, preferably at least 50% and more preferably at least 70%, formed by methods such as described, for example, in U.S. Pat. No. 4,152,499 and W. German Offenlegungsschrift 29 04 314, are also suitable for use in forming the long chain substituted phenol reactant.

The alkylation of the substituted hydroxyaromatic compound is typically performed in the presence of an alkylating catalyst such as BF_3 at a temperature in the range of about 50 to about 200°C. The long chain alkyl substituents on the benzene ring of the phenolic compound are derived from polyolefin having a number average molecular weight

(Mn) of from about 500 to about 3000 (preferably from about 500 to about 2000) as determined by GPC. It is also preferred that the polyolefin used have a polydispersity in the range of about 1 to about 4 (preferably from about 1 to about 2) as determined by GPC.

The preferred configuration of the substituted hydroxyaromatic compound is that of a hydrocarbyl substituent in the para-position and the C₁₋₄ alkyl substituent in one of the ortho-positions. However, any alkylphenol readily reactive in the Mannich condensation reaction may be employed. The long chain hydrocarbyl substituents may contain some residual unsaturation, but in general, are substantially saturated.

A very important feature of this invention is the use of an aliphatic polyamine having one and only one primary or secondary amino group in the molecule capable of entering into the Mannich condensation reaction with the substituted phenolic compound and the aldehyde. The other amino group(s) is/are usually tertiary or quaternary ammonium groups, preferably a single tertiary amino group. However, there can be one or more secondary amino groups that are sterically hindered to such an extent as to be substantially incapable of directly participating in the Mannich condensation reaction. The use of the above-specified reactant ratios together with the use of the type of polyamines referred to herein has been shown to result in the provision of novel Mannich base products having excellent performance capabilities and physical properties.

Representative amine reactants are alkylene polyamines having, inter alia, a single suitably reactive primary or secondary amino group in the molecule. Other substituents such as hydroxyl, cyano, amido, etc., can be present in the polyamine. Preferably the amine is an aliphatic diamine having one primary or secondary amino group and one tertiary amino group in the molecule. Examples of suitable polyamines include N,N,N',N''-tetraalkyldialkylenetriamines (two terminal tertiary amino groups and one central secondary amino group), N,N,N',N''-tetraalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal primary amino group), N,N,N',N''-pentaalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal secondary amino group), N,N-dihydroxyalkyl- α,ω -alkylenediamines (one terminal tertiary amino group and one terminal primary amino group), N,N,N'-trihydroxyalkyl- α,ω -alkylenediamines (one terminal tertiary amino group and one terminal secondary amino group), tris(dialkylaminoalkyl)aminoalkylmethanes (three terminal tertiary amino groups and one terminal primary amino group), and like compounds, wherein the alkyl groups are the same or different and typically contain no more than about 12 carbon atoms each, and which preferably contain from 1 to 4 carbon atoms each. Most preferably these alkyl groups are methyl and/or ethyl groups. Preferred polyamine reactants are N,N-dialkyl- α,ω -alkylenediamine, such as those having from 3 to about 6 carbon atoms in the alkylene group and from 1 to about 12 carbon atoms in each of the alkyl groups, which most preferably are the same but which can be different. Most preferred is N,N-dimethyl-1,3-propanediamine.

Examples of polyamines having one reactive primary or secondary amino group that can participate in the Mannich condensation reaction, and at least one sterically hindered amino group that cannot participate directly in the Mannich condensation reaction to any appreciable extent include N-(tert-butyl)-1,3-propanediamine, N-neopentyl-1,3-propanediamine, N-(tert-butyl)-1-methyl-1,2-ethanediamine, N-(tert-butyl)-1-methyl-1,3-propanediamine, and 3,5-di(tert-butyl)aminoethylpiperazine.

Representative aldehydes for use in the preparation of the Mannich base products include the aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, heptaldehyde, stearaldehyde. Aromatic aldehydes which may be used include benzaldehyde and salicylaldehyde. Illustrative heterocyclic aldehydes for use herein are furfural and thiophene aldehyde, etc. Also useful are formaldehyde-producing reagents such as paraformaldehyde, or aqueous formaldehyde solutions such as formalin. Most preferred is formaldehyde or formalin.

The condensation reaction among the alkylphenol, the specified amine(s) and the aldehyde is conducted at a temperature in the range of about 40 to about 200°C. The reaction can be conducted in bulk (no diluent or solvent) or in a solvent or diluent. Water is evolved and can be removed by azeotropic distillation during the course of the reaction.

As noted above, another very important feature of this invention is the proportions of the reactants maintained in the Mannich condensation reaction mixture, viz., from 0.8 to 1.5 mole part(s) of at least one aliphatic polyamine of the type described above, and from 0.8 to 1.3 mole part(s) of at least one aldehyde, with the proviso that the mole ratio of aldehyde to amine is 1.2:1 or less. An especially preferred embodiment involves use of N,N-dimethyl-1,3-propanediamine as the polyamine, formaldehyde as the aldehyde, and a molar ratio of the above predominately monoalkylated phenol to N,N-dimethyl-1,3-propanediamine to formaldehyde of 1:1-1.15:0.90-1.20, respectively, with the proviso that if the molar quantity of formaldehyde is larger than the molar quantity of the amine, the excess molar amount of the formaldehyde does not exceed about 0.1. The most preferred molar ratio for these last-named reactants is about 1 mole of the N,N-dimethyl-1,3-propanediamine and about 1.05 mole of formaldehyde per mole of the above predominately monoalkylated phenol. When performing the reactions on a laboratory scale the foregoing ratios are relatively easy to maintain and control. However, when performing the reaction in large scale plant reactors, the possibility of losses of the more volatile reactants (amine and formaldehyde) can be encountered, as by vaporization into the reactor headspace, entrainment in purge streams as water is being purged from the reaction mixture, etc. Thus when con-

ducting the reaction on a large scale care should be exercised to compensate for any such losses so that the liquid reaction mixture actually contains the reactants in the proportions utilized pursuant to this invention.

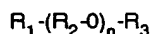
Liquid Carriers

The Mannich base products of this invention are preferably used in combination with a liquid carrier or induction aid. Such carriers can be of various types, such as for example liquid poly- α -olefin oligomers, liquid polyalkene hydrocarbons (e.g., polypropene, polybutene, polyisobutene, or the like), liquid hydrotreated polyalkene hydrocarbons (e.g., hydrotreated polypropene, hydrotreated polybutene, hydrotreated polyisobutene, or the like), mineral oils, liquid poly(oxyalkylene) compounds, liquid alcohols or polyols, liquid esters, and similar liquid carriers or solvents. Mixtures of two or more such carriers or solvents can be employed.

Preferred liquid carriers because of their performance capabilities are 1) a mineral oil or a blend of mineral oils that have a viscosity index of less than about 120, 2) one or a blend of poly- α -olefin oligomers, 3) one or more poly(oxyalkylene) compounds having an average molecular weight in the range of about 500 to about 3000, or 4) a mixture of any two or all three of 1), 2) and 3). The mineral oil carriers that can be used include paraffinic, naphthenic and asphaltic oils, and can be derived from various petroleum crude oils and processed in any suitable manner. For example, the mineral oils may be solvent extracted or hydrotreated oils. Reclaimed mineral oils can also be used. Hydrotreated oils are the most preferred. Preferably the mineral oil used has a viscosity at 40°C. of less than about 1600 SUS, and more preferably between about 300 and 1500 SUS at 40°C. Paraffinic mineral oils most preferably have viscosities at 40°C in the range of about 475 SUS to about 700 SUS. For best results it is highly desirable that the mineral oil have a viscosity index of less than about 100, more preferably, less than about 70 and most preferably in the range of from about 30 to about 60.

The poly- α -olefins (PAO) which are included among the preferred carrier fluids are the hydrotreated and unhydrotreated poly- α -olefin oligomers, i.e., hydrogenated or unhydrogenated products, primarily trimers, tetramers and pentamers of α -olefin monomers, which monomers contain from 6 to 12, generally 8 to 12 and most preferably about 10 carbon atoms. Their synthesis is outlined in Hydrocarbon Processing, Feb. 1982, page 75 et seq., and in U.S. Pat. Nos. 3,763,244; 3,780,128; 4,172,855; 4,218,330; and 4,950,822. The usual process essentially comprises catalytic oligomerization of short chain linear alpha olefins (suitably obtained by catalytic treatment of ethylene). The poly- α -olefins used as carriers will usually have a viscosity (measured at 100°C) in the range of 2 to 20 centistokes (cSt). Preferably, the poly- α -olefin has a viscosity of at least 8 cSt, and most preferably about 10 cSt at 100°C.

The poly(oxyalkylene) compounds which are among the preferred carrier fluids for use in this invention are fuel-soluble compounds which can be represented by the following formula



wherein R_1 is typically a hydrogen, alkoxy, cycloalkoxy, hydroxy, amino, hydrocarbyl (e.g., alkyl, cycloalkyl, aryl, alkylaryl, aralkyl, etc.), amino-substituted hydrocarbyl, or hydroxy-substituted hydrocarbyl group, R_2 is an alkylene group having 2-10 carbon atoms (preferably 2-4 carbon atoms), R_3 is typically a hydrogen, alkoxy, cycloalkoxy, hydroxy, amino, hydrocarbyl (e.g., alkyl, cycloalkyl, aryl, alkylaryl, aralkyl, etc.), amino-substituted hydrocarbyl, or hydroxy-substituted hydrocarbyl group, and n is an integer from 1 to 500 and preferably in the range of from 3 to 120 representing the number (usually an average number) of repeating alkyleneoxy groups. In compounds having multiple $-R_2-O-$ groups, R_2 can be the same or different alkylene group and where different, can be arranged randomly or in blocks. Preferred poly(oxyalkylene) compounds are monools comprised of repeating units formed by reacting an alcohol with one or more alkylene oxides, preferably one alkylene oxide.

The average molecular weight of the poly(oxyalkylene) compounds used as carrier fluids is preferably in the range of from about 500 to about 3000, more preferably from about 750 to about 2500, and most preferably from above about 1000 to about 2000.

One useful sub-group of poly(oxyalkylene) compounds is comprised of the hydrocarbyl-terminated poly(oxyalkylene) monools such as are referred to in the passage at column 6, line 20 to column 7 line 14 of U.S. Pat. No. 4,877,416 and references cited in that passage, said passage and said references being incorporated herein by reference as if fully set forth.

A preferred sub-group of poly(oxyalkylene) compounds is comprised of one or a mixture of alkylpoly(oxyalkylene) monools which in its undiluted state is a gasoline-soluble liquid having a viscosity of at least about 70 centistokes (cSt) at 40°C and at least about 13 cSt at 100°C. Of these compounds, monools formed by propoxylation of one or a mixture of alkanols having at least about 8 carbon atoms, and more preferably in the range of about 10 to about 18 carbon atoms, are particularly preferred.

The poly(oxyalkylene) carriers used in the practice of this invention preferably have viscosities in their undiluted

state 1 at least about 60 cSt at 40°C (more preferably at least about 70 cSt at 40°C) and at least about 11 cSt at 100°C (more preferably at least about 13 cSt at 100°C). In addition, the poly(oxyalkylene) compounds used in the practice of this invention preferably have viscosities in their undiluted state of no more than about 400 cSt at 40°C and no more than about 50 cSt at 100°C. More preferably, their viscosities will not exceed about 300 cSt at 40°C and will not exceed about 40 cSt at 100°C. The most preferred poly(oxyalkylene) compounds will have viscosities of no more than about 200 cSt at 40°C, and no more than about 30 cSt at 100°C.

Preferred poly(oxyalkylene) compounds are poly(oxyalkylene) glycol compounds and monoether derivatives thereof that satisfy the above viscosity requirements and that are comprised of repeating units formed by reacting an alcohol or polyalcohol with an alkylene oxide, such as propylene oxide and/or butylene oxide with or without use of ethylene oxide, and especially products in which at least 80 mole % of the oxyalkylene groups in the molecule are derived from 1,2-propylene oxide. Details concerning preparation of such poly(oxyalkylene) compounds are referred to, for example, in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, Volume 18, pages 633-645 (Copyright 1982 by John Wiley & Sons), and in references cited therein, the foregoing excerpt of the Kirk-Othmer encyclopedia and the references cited therein being incorporated herein in toto by reference. U.S. Patent Nos. 2,425,755; 2,425,845; 2,448,664; and 2,457,139 also describe such procedures, and are also incorporated herein by reference as if fully set forth herein.

A particularly preferred sub-group of poly(oxyalkylene) compounds is comprised of one or a mixture of alkylpoly(oxyalkylene)monools which in its undiluted state is a gasoline-soluble liquid having a viscosity of at least about 70 centistokes (cSt) at 40°C and at least about 13 cSt at 100°C. Typically the maximum viscosities at these temperatures are no more than about 400 cSt at 40°C and no more than about 50 cSt at 100°C. More preferably, their viscosities will not exceed about 300 cSt at 40°C and will not exceed about 40 cSt at 100°C. The most preferred poly(oxyalkylene) compounds will have viscosities of no more than about 200 cSt at 40°C, and no more than about 30 cSt at 100°C. Of these compounds, monools formed by propoxylation of one or a mixture of alkanols having at least about 8 carbon atoms, and more preferably in the range of about 10 to about 18 carbon atoms, are particularly preferred.

The poly(oxyalkylene) compounds used pursuant to this invention will contain a sufficient number of branched oxyalkylene units (e.g., methyltrimethyleneoxy units and/or ethyltrimethyleneoxy units) to render the poly(oxyalkylene) compound gasoline soluble.

Another group of preferred carriers is the liquid polyalkylenes such as polypropylenes, polybutenes, polyisobutylenes, polyamylenes, copolymers of propene and butene, copolymers of butene and isobutene, copolymers of propene and isobutene, copolymers of propene, butene and isobutene, and the like. Use of materials of this general type together with other carrier fluids is described for example, in U.S. Pat. Nos. 5,089,028 and 5,114,435, the disclosures of which are incorporated herein by reference.

In some cases, the Mannich base detergent/dispersant can be synthesized in the carrier fluid. In other instances, the preformed detergent/dispersant is blended with a suitable amount of the carrier fluid. If desired, the detergent/dispersant can be formed in a suitable solvent or carrier fluid and then blended with an additional quantity of the same or a different carrier fluid.

Additive Proportions

The proportion of the liquid carrier used relative to the Mannich base in the preferred additive packages and fuel compositions of this invention is such that the fuel composition when consumed in an engine results in improved intake valve cleanliness as compared intake valve cleanliness of the same engine operated on the same composition except for being devoid of the liquid carrier. Thus in general, the weight ratio of carrier fluid to Mannich base detergent/dispersant on an active ingredient basis, i.e. excluding solvent(s), if any, used in the manufacture of the Mannich base either during or after its formation but before addition of the carrier fluid, will usually fall within the range of about 0.3:1 to about 2.0:1, and preferably within the range of about 0.6:1 to about 1.5:1.

Typically the additive concentrates of this invention contain from about 12 to about 69 wt %, and preferably from about 22 to about 50 wt % of the Mannich base detergent/dispersant on an active ingredient basis (see the immediately preceding paragraph for a definition of this term). The additive concentrates also contain carrier fluid, the level of which is determined by the desired carrier to Mannich base detergent/dispersant ratio. If desired, the additive concentrates may contain small amounts (e.g., a total of up to about 10 wt % and preferably a total of up to about 5 wt % based on the total weight of the additive concentrate), of one or more fuel-soluble antioxidants, demulsifying agents, rust or corrosion inhibitors, metal deactivators, combustion modifiers, alcohol cosolvents, octane improvers, emission reducers, friction modifiers, lubricity additives, ancillary detergent/dispersant additives, marker dyes, and the like. Multifunctional additives such as cyclopentadienyl manganese tricarbonyl compounds (e.g., methylcyclopentadienyl manganese tricarbonyl) can also be included in the additive concentrates.

When formulating the fuel compositions of this invention, the Mannich product and carrier fluid (with or without other additives) are employed in amounts sufficient to reduce or inhibit deposit formation in an internal combustion

engine. Thus the fuels will contain minor amounts of the Mannich base detergent/dispersant and of the liquid carrier fluid proportioned as above that control or reduce formation of engine deposits, especially intake system deposits, and most especially intake valve deposits in spark-ignition internal combustion engines. Generally speaking the fuels of this invention will contain on an active ingredient basis as defined above, an amount of the Mannich base detergent/dispersant in the range of about 5 to about 150 ptb (pounds by weight of additive per thousand barrels by volume of fuel), and preferably in the range of about 10 to about 100 ptb. In the preferred fuel compositions wherein a liquid carrier fluid is used, the amount of the liquid carrier fluid will usually fall in the range of about 5 ptb to about 225 ptb, and preferably will be in the range of about 10 ptb to about 150 ptb. Other additives, such as one or more fuel-soluble antioxidants, demulsifying agents, rust or corrosion inhibitors, metal deactivators, combustion modifiers, alcohol co-solvents, octane improvers, emission reducers, friction modifiers, lubricity additives, ancillary detergent/dispersant additives, marker dyes, and multifunctional additives (e.g., methylcyclopentadienyl manganese tricarbonyl and/or other cyclopentadienyl manganese tricarbonyl compounds) can also be included in the fuels of this invention. These manganese compounds are among particularly preferred additional additives in the compositions of this invention because of their outstanding ability to reduce tailpipe emissions such as NOx and smog forming precursors, and to significantly improve the octane quality of fuel compositions, such as gasolines of the traditional types and of the newer "reformulated" types. Whatever components are selected for use in the compositions of this invention, each component should be present in an amount at least sufficient for it to exert its intended function or functions in the finished fuel composition.

The base fuels used in formulating the fuels of this invention are any and all base fuels suitable for use in the operation of spark ignition internal combustion engines such as unleaded motor and aviation gasolines, and so-called reformulated gasolines which typically contain both hydrocarbons of the gasoline boiling range and fuel-soluble oxygenated blending components such as alcohols, ethers, and other suitable oxygen-containing organic compounds. Preferred blending agents include fuel-soluble alkanols such as methanol, ethanol, and their higher homologs, and fuel-soluble ethers such as methyl tertiary butyl ether, ethyl tertiary butyl ether, methyl tertiary amyl ether, and analogous compounds and mixtures of such materials. Oxygenates, when used, will normally be present in the base fuel in an amount below about 25 % by volume, and preferably in an amount that provides an oxygen content in the overall fuel in the range of about 0.5 to about 5 percent by volume. However in the practice of this invention departures from these ranges of proportions are permissible whenever deemed necessary, appropriate or desirable.

The additives used in formulating the preferred fuels of this invention can be blended into the base fuel individually or in various subcombinations. However, it is definitely preferable to blend all of the components concurrently using an additive concentrate of this invention as this takes advantage of the mutual compatibility afforded by the combination of ingredients when in the form of an additive concentrate. Also use of a concentrate reduces blending time and lessens the possibility of blending errors.

EXAMPLES

The practice and advantages of this invention are demonstrated by the following examples which are presented for purposes of illustration and not limitation. In each Mannich condensation reaction the following general procedure was used. The Mannich reaction products of the present invention were derived by reaction among long chain alkylated ortho-cresol ("PBP"), N,N-dimethyl-1,3-propanediamine ("DMPD"), and formaldehyde ("FA"). The PBP was formed by reacting ortho-cresol with a polyolefin indicated in Table 2. The Mannich reaction products outside of the scope of the present invention were derived by reaction among long chain alkylated phenol ("PBP"), DMPD or diethylene triamine ("DETA"), and FA. The PBP and DMPD/DETA were added to a resin kettle equipped with mechanized stirring, nitrogen feed, a Dean-Stark trap, and a heating mantle. Solvent, Aromatic 100 at 25 % by weight of product, was introduced and the mixture was heated to 50°C along with a slight exotherm. Next, 37 % formaldehyde solution was added gradually, while vigorous stirring was maintained. A second, mild exotherm was noted. The reaction mixture was heated to reflux; about 102°C. The azeotropic blend of water and solvent was removed continuously over a period lasting one hour. The temperature was increased as required to sustain removal of water, then the reaction mixture was heated gradually to 150°C, while sparging with nitrogen. After reaction the viscous product mixture was weighed and diluted with Aromatic 100 solvent as desired.

The activity of the product mixtures was determined by chromatographic separation. A 2-gram sample is separated on a silica gel column (40g of 60-200 mesh). The inactive components and alkylphenols are eluted from the column with n-hexane (400mL) and methylene chloride (400mL) respectively. The active Mannich components adhere to the gel, and can only be quantified by difference after all of the eluants are evaporated to dryness. The percentage of converted polyalkylphenol is calculated directly from the activity of the starting material and the weight fraction of polyalkylphenol in the product. Conversions for each example are given in Table 2. "PBP Activity" indicates how much of the polyolefin was reacted onto the hydroxyaromatic compound to form a substituted hydroxyaromatic compound. "% PBP Conversion" indicates how much of the substituted hydroxyaromatic compound reacted with the amine to form the Mannich product.

Using the above generalized procedure various Mannich products were prepared from PBP, DMPD or DETA and FA. Table 2 summarizes the relevant information and data. In those cases where a result is not available because the component was not present or the analysis was not conducted on the particular product, the designation "N/A" is used in the table. The examples outside the scope of the present invention ("Comparative Examples") are either Mannich products derived from a long chain alkylated phenol (Examples 1, 3, 4, and 7) or base fuel (Example 8) having no detergent added.

Gasoline fuel compositions were subjected to engine tests whereby the substantial effectiveness of these compositions in minimizing intake valve deposit weight was conclusively demonstrated. The Mannich reaction products were combined with a polypropylene glycol carrier fluid and these components were added to the gasoline in amounts indicated in Table 2. The specifications of the different gasolines used are set forth in Table 1. The test series was performed using a Ford 2.3-liter engine operated either on a test stand or on a mileage accumulation dynamometer under standard operating conditions for determination of deposit formation on intake valves. The polyolefins used to form the Mannich products in Table 2 are high reactivity polyisobutylene having an alkylvinylidene isomer content of 80% and a number average molecular weight of about 1000 (HR-PIB), polyisobutylene having an alkylvinylidene isomer content of less than 10% and a number average molecular weight of about 900 (PIB), and polypropylene having a molecular weight of about 800 (PP).

TABLE 1

Fuel Profiles			
	FUEL A	FUEL B	FUEL C
Bromine Number ASTM D1159	37.08	26.50	32.17
Aromatics, Vol% ASTM D1319	21.1	26.9	25.2
Olefins, Vol% ASTM D1319	17.3	16.3	15.0
Saturates, Vol% ASTM D1319	61.6	56.8	59.8
Sulfur, Wt% ASTM D4294	0.039	0.059	0.053
MTBE, Vol% ASTM D4815-89	0.29	0.26	0.42
Initial Boiling Point °F ASTM D86	89	96	87
End Point °F ASTM D86	401	433	424

TABLE 2

Ex. No.	Polyolefin	Head Group	Amine	PBP Activity	% PBP Conversion	Carrier	Mannich, ptb	Carrier, ptb	IVD, mg	Fuel
1*	PIB	phenol	DMPD	76.16	87.85	D-21	40	32	108.10	A
2	HR-PIB	cresol	DMPD	88.39	94.34	D-21	32.1	32	33.30	A
3*	PIB	phenol	DMPD	76.16	85.93	D-21	39.6	32	41.90	B
4*	HR-PIB	phenol	DMPD	88.39	91.80	D-21	35.3	32	42.00	B
5	HR-PIB	cresol	DMPD	88.39	94.34	D-21	32.1	32	17.20	B
6	PIB	cresol	DMPD	74.5	91.77	AR-22	32.39	35	44.50	C
7*	PP	phenol	DETA	76.3	N/A	AR-22	35	35	75.40	C
8*	none	none	none	N/A	N/A	none	none	none	271	C

* Comparative Examples

Upon examination of Table 2, it is clear that the PBPs prepared from HR-PIB (Examples 2, 4*, and 5) exhibit significantly higher values for PBP activity than PBPs prepared from either PIB or PP (Examples 1*, 3*, 6, and 7), regardless of the head group, i.e., cresol or phenol. This indicates that more of the polyolefin is reacted onto the head group when HR-PIB is used compared to PBPs where PIB or PP are used. Further, upon reaction of the PBP with

formaldehyde and the amine to form the Mannich product it is clear that PBPs prepared from ortho-cresol (Examples 2, 5, and 6) exhibit significantly higher conversions to the Mannich reaction product compared with similar Mannichs derived from phenol (Examples 1*, 3*, 4*, and 7). This indicates that more of the amine is actually reacted onto the hydroxyaromatic compound and correspondingly, less unreacted amine remains.

5 The improvements in reducing intake valve deposit formation obtained by using ortho-cresol as the starting hydroxyaromatic material, rather than phenol, are evident upon comparison of Examples 2, 5 and 6, which use ortho-cresol as the head group and are thus examples within the scope of the present invention, and Examples 1*, 3*, 4*, 7* and 8* which use phenol as the head group and are therefore outside the scope of the present invention.

10 It is to be understood that the reactants and components referred to by chemical name anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (e.g., base fuel, solvent, etc.). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together either in performing a desired chemical reaction (such as a Mannich condensation reaction) or in forming a desired composition (such as an additive concentrate or additized fuel blend). It will also be recognized that the additive components can be added or blended into or with the base fuels individually per se and/or as components used in forming preformed additive combinations and/or subcombinations. Likewise preformed additive concentrates, in which higher proportions of the additive components are blended together usually with one or more diluents or solvents, can be formed so that subsequently the concentrate can be blended with a base fuel in the course of forming the finished fuel composition. Accordingly, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, component or ingredient as it exists or may have existed at the time just before it was first blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. The fact that the substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of such blending or mixing operations is thus wholly immaterial for an accurate understanding and appreciation of this disclosure and the claims thereof.

25 As used herein the term "fuel-soluble" means that the substance under discussion should be sufficiently soluble at 20°C in the base fuel selected for use to reach at least the minimum concentration required to enable the substance to serve its intended function. Preferably the substance will have a substantially greater solubility in the base fuel than this. However, the substance need not dissolve in the base fuel in all proportions.

Each and every patent or other publication referred to in any portion of this specification is incorporated in toto into this disclosure by-reference for all purposes, as if fully set forth herein.

30 This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove. Rather, what is intended to be covered is as set forth in the ensuing claims and the equivalents thereof permitted as a matter of law.

40 Claims

1. A Mannich product composition formed from (i) one mole part of at least one substituted hydroxyaromatic compound having on the ring both (a) an aliphatic hydrocarbyl substituent derived from a polyolefin having a number average molecular weight in the range of about 500 to about 3000, and (b) a C₁₋₄ alkyl; (ii) from 0.8 to 1.5 mole part(s) of at least one aliphatic polyamine having one and only one primary or secondary amino group in the molecule; and (iii) from 0.8 to 1.3 mole part(s) of at least one aldehyde, with the proviso that the mole ratio of aldehyde to amine is 1.2:1 or less.
2. A composition in accordance with Claim 1 wherein the composition is formed by heating a mixture of (i), (ii) and (iii) at a temperature above about 40°C at which a Mannich condensation reaction takes place.
3. A composition in accordance with Claim 1 or Claim 2 wherein the hydroxyaromatic compound is one mole part of a substituted phenol in which the hydrocarbyl substituent is derived from polypropylene, polybutylene or a copolymer of propylene and butylene having a number average molecular weight in the range of about 500 to about 3000 and a polydispersity in the range of about 1 to about 4, wherein the polyamine is from 0.8 to 1.2 mole part(s) of one or more N,N-dialkyl- α,ω -alkylene-diamines in which the alkylene group has at least 3 carbon atoms, and wherein the aldehyde is from 0.8 to 1.2 mole part(s) of formaldehyde, provided the mole ratio of formaldehyde to said diamine(s) is 1.2:1 or less.

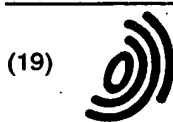
4. A composition in accordance with Claim 1 or Claim 2 wherein the hydroxyaromatic compound is a substituted phenol in which the hydrocarbyl substituent is derived from polypropylene, polybutylene or a copolymer of propylene and butylene having a number average molecular weight in the range of about 500 to about 3000 and a polydispersity in the range of about 1 to about 4, wherein the polyamine is N,N-dimethyl-1,3-propanediamine, wherein the aldehyde is formaldehyde, and wherein the mole ratio of the substituted phenol to N,N-dimethyl-1,3-propanediamine to formaldehyde used in forming said product composition is 1:1-1.15:0.90-1.20, respectively, with the proviso that if the molar quantity of formaldehyde used is larger than the molar quantity of the amine used, the excess molar amount of the formaldehyde does not exceed about 0.1.
5. A composition in accordance with Claim 4 wherein said mole ratio is about 1 mole of the N,N-dimethyl-1,3-propanediamine and about 1.05 mole of formaldehyde per mole of the substituted phenol.
6. A composition in accordance with any one of Claims 1 to 5 wherein the hydrocarbyl substituent (a) of the substituted phenol is derived from polybutylene and the C₁₋₄ alkyl (b) is methyl.
7. A composition in accordance with Claim 6 wherein at least about 20 percent of the total polybutylene comprises an alkylvinylidene isomer.
8. A fuel additive composition which comprises:
 - a) a detergent/dispersant fuel-soluble Mannich product composition according to any one of Claims 1 to 7, and
 - b) at least one liquid carrier for said detergent/dispersant in proportions such that for each part by weight of detergent/dispersant on an active ingredient basis there is in the range of about 0.3 to about 2.0 parts by weight of liquid carrier therefor.
9. A composition in accordance with Claim 8 wherein the liquid carrier is at least one fuel-soluble poly(oxyalkylene) compound.
10. A composition in accordance with Claim 9 wherein the weight ratio of said at least one poly(oxyalkylene) compound to the detergent/dispersant on an active ingredient basis is 2.0:1.0 or less.
11. A composition in accordance with Claim 9 or 10 wherein said poly(oxyalkylene) compound is at least one poly(oxypropylene) monool from 1,2-propylene oxide and one or more primary alcohols having at least 8 carbon atoms per molecule.
12. A composition in accordance with Claim 11 wherein said at least one monool has a kinematic viscosity in its undiluted state of at least 70 cSt at 40°C and at least about 13 cSt at 100°C.
13. A composition in accordance with any one of Claims 8 to 12 further comprising at least one inert hydrocarbon solvent that has a boiling point or boiling range below about 200°C.
14. A fuel composition for use in spark ignition internal combustion engines into which has been blended from about 5 to about 200 ptb of a composition of any one of Claims 1 to 7.
15. A fuel composition for use in spark ignition internal combustion engines into which has been blended a detergent/dispersant composition in accordance with any one of Claims 8 to 13 in an amount at least sufficient to reduce or minimize the weight of intake valve deposits in a spark ignition internal combustion engine operated on said fuel composition.
16. A method of minimizing or reducing intake valve deposits in a spark ignition internal combustion engine which comprises providing as fuel for the operation of the engine, a fuel composition in accordance with Claim 15.
17. A method of minimizing or reducing intake valve sticking in a spark ignition internal combustion engine which comprises providing as fuel for the operation of the engine, a fuel composition in accordance with Claim 15.
18. A Mannich product composition formed (A) one mole part of at least one substituted hydroxyaromatic compound having on the ring both (a) an aliphatic hydrocarbyl substituent derived from a polyolefin having a number average molecular weight in the range of about 500 to about 3000, and (b) a C₁₋₄ alkyl; (B) from 0.8 to 1.3 mole part(s) of

at least one aldehyde; and (C) from 0.8 to 1.5 mole part(s) of at least one aliphatic polyamine with the provisos that:

(1) the mole ratio of aldehyde to amine is 1.2:1 or less; and

(2) the polyamine used in forming said composition has in the molecule one primary or secondary amino group capable of undergoing a Mannich condensation reaction with (A) and (B), the other amino group or groups in the molecule being substantially inert toward direct participation in such Mannich condensation reaction.

19. A composition in accordance with Claim 18 wherein the composition is formed by heating a mixture of (A), (B) and (C) at a temperature above about 40°C at which a Mannich condensation reaction takes place; wherein the substituted hydroxyaromatic compound is one mole part of a substituted phenol in which the hydrocarbyl substituent is derived from polypropylene, polybutylene or a copolymer of propylene and butylene having a number average molecular weight in the range of about 500 to about 3000 and a polydispersity in the range of about 1 to about 4; wherein the polyamine is from 0.8 to 1.2 mole part(s) of one or more N,N-dialkyl- α,ω -alkylenediamines in which the alkylene group has at least 3 carbon atoms; and wherein the aldehyde is from 0.8 to 1.2 mole part(s) of formaldehyde, provided the mole ratio of formaldehyde to said diamine(s) is 1.2:1 or less.
20. A composition in accordance with Claim 18 wherein the composition is formed by heating a mixture of (A), (B) and (C) at a temperature above about 40°C at which a Mannich condensation reaction takes place; wherein the substituted hydroxyaromatic compound is a substituted phenol in which the hydrocarbyl substituent is derived from polypropylene, polybutylene or a copolymer of propylene and butylene having a number average molecular weight in the range of about 500 to about 3000 and a polydispersity in the range of about 1 to about 4; wherein the polyamine is N,N-dimethyl-1,3-propanediamine, wherein the aldehyde is formaldehyde; and wherein the mole ratio of the substituted phenol to N,N-dimethyl-1,3-propanediamine to formaldehyde used in forming said product composition is 1:1-1.15:0.90-1.20, respectively, with the proviso that if the molar quantity of formaldehyde used is larger than the molar quantity of the amine used, the excess molar amount of the formaldehyde does not exceed about 0.1.
21. A composition in accordance with Claim 20 wherein said mole ratio is about 1 mole of the N,N-dimethyl-1,3-propanediamine and about 1.05 mole of formaldehyde per mole of the substituted phenol, and wherein the hydrocarbyl substituent (a) of the substituted phenol is derived from polybutylene and the C₁₋₄ alkyl (b) is methyl.
22. A composition in accordance with Claim 21 wherein at least about 20 percent of the total polybutylene comprises an alkylvinylidene isomer.



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 870 819 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
16.06.1999 Bulletin 1999/24

(51) Int Cl.⁶ **C10L 1/22, C10L 1/14,
C10L 10/00**

(43) Date of publication A2:
14.10.1998 Bulletin 1998/42

(21) Application number: 98302812.7

(22) Date of filing: 09.04.1998

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 10.04.1997 US 837246

(71) Applicant: **ETHYL CORPORATION**
Richmond, Virginia 23219-4304 (US)

(72) Inventors:
• **Malfer, Dennis J.**
Glen Allen, Virginia 23060 (US)
• **Franklin, Randall M.**
Mechanicsville, Virginia 23116 (US)
• **Colucci, William L.**
Glen Allen, Virginia 23060 (US)

(74) Representative: **Smaggasgale, Gillian Helen et al**
Mathys & Squire,
100 Gray's Inn Road
London WC1X 8AL (GB)

(54) **Additives for minimizing intake valve deposits, and their use**

(57) New, highly effective detergent/dispersants for use in spark ignition fuels are described. They are Mannich condensation products formed from (i) one mole part of at least one substituted hydroxyaromatic compound having on the ring both (a) an aliphatic hydrocarbyl substituent derived from a polyolefin having a number average molecular weight in the range of about 500 to about 3000, and (b) a C₁₋₄ alkyl; (ii) from 0.8 to 1.5 mole part(s) of aliphatic polyamine having one and

only one primary or secondary amino group in the molecule capable of participating in the Mannich condensation reaction; and (iii) from 0.8 to 1.3 mole part(s) of aldehyde, provided that the mole ratio of aldehyde to amine is 1.2:1 or less. Carrier fluids such as poly(oxyalkylene) compounds further enhance the effectiveness of these Mannich condensation products in minimizing or reducing intake valve deposits and/or intake valve sticking.

EP 0 870 819 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 30 2812

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	EP 0 811 672 A (ETHYL) 10 December 1997 * page 3, line 33 - line 36 *	1-22	C10L1/22 C10L1/14 C10L10/00
X	EP 0 647 700 A (ETHYL) 12 April 1995	1,2,6, 8-16,18	
Y	* page 4, line 1 - line 42; claims 1,2,4-10,12-16 *	7	
Y	* page 5, line 51 - line 55 *		
Y	WO 94 14739 A (CHEVRON) 7 July 1994 * the whole document *	7	
X	US 3 649 229 A (OTTO) 14 March 1972	1,2,6, 14,18	
Y	* column 1, line 63 - line 70; claim 1; example 2 *	8-13, 15-17	
Y	EP 0 588 429 A (SHELL) 23 March 1994 * page 6, line 43 - line 47 * * page 12, line 53 - page 13, line 1 *	8-13, 15-17	
A	DE 22 09 579 B (ETHYL) 26 July 1973 * the whole document *	1-22	C10L
A	EP 0 440 507 A (EXXON) 7 August 1991 * page 2, line 1 - line 2 * * page 8, line 15 - line 23 * * page 9, line 34 - line 37 * * page 14, line 34 - line 36 *	1-22	
A	US 5 334 775 A (GUTIERREZ ET AL.) 2 August 1994 * the whole document *	3,4,7, 19-22	
A	US 3 994 698 A (WORREL) 30 November 1976 * the whole document *	1-22	
	-/--		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27 April 1999	Examiner De La Morinerie, B
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>			

E-P-O-F-3/4/4 1503 L3 B2 (P04C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 30 2812

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 4 116 644 A (JACKISCH ET AL.) 26 September 1978 * column 4, line 38 - column 5, line 39; claim 1 *	1-22	
A	CA 2 089 833 A (SHELL) 21 August 1993 * the whole document *	1-22	
A	GB 2 010 324 A (CHEVRON) 27 June 1979 * page 1, line 121 - line 122 * * page 3, line 1 - line 22 * * page 8, line 40 - line 41 *	1-22	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27 April 1999	Examiner De La Morinerie, B
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/92 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 30 2812

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

27-04-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 811672	A	10-12-1997	US 5634951 A	03-06-1997
			AU 2473097 A	11-12-1997
			JP 10060460 A	03-03-1998
			SG 50843 A	20-07-1998
			US 5725612 A	10-03-1998

EP 647700	A	12-04-1995	AU 678514 B	29-05-1997
			AU 7445294 A	27-04-1995
			CA 2133796 A	07-04-1995
			JP 2744205 B	28-04-1998
			JP 7197052 A	01-08-1995
			US 5697988 A	16-12-1997

WO 9414739	A	07-07-1994	US 5300701 A	05-04-1994
			AT 163911 T	15-03-1998
			AU 676710 B	20-03-1997
			AU 5956494 A	19-07-1994
			BR 9305986 A	21-10-1997
			CA 2130838 A	29-06-1994
			DE 69317410 D	16-04-1998
			DE 69317410 T	02-07-1998
			EP 0628022 A	14-12-1994
			JP 7507073 T	03-08-1995

US 3649229	A	14-03-1972	NONE	

EP 588429	A	23-03-1994	AT 164388 T	15-04-1998
			AU 663618 B	12-10-1995
			AU 4731393 A	24-03-1994
			BR 9303765 A	03-05-1994
			CA 2104825 A	15-03-1994
			CN 1084208 A,B	23-03-1994
			DE 69317614 D	30-04-1998
			DE 69317614 T	10-09-1998
			DK 588429 T	11-05-1998
			FI 933927 A	15-03-1994
			JP 6184568 A	05-07-1994
			NO 933263 A	15-03-1994
			NZ 248495 A	26-08-1994
			SG 47654 A	17-04-1998
			ZA 9306727 A	05-04-1994

DE 2209579	B	26-07-1973	US 3948619 A	06-04-1976
			CA 966309 A	22-04-1976
			US 3994698 A	30-11-1976

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 30 2812

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

27-04-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 440507	A	07-08-1991	US 5200103 A	06-04-1993
			CA 2034760 A	02-08-1991
			DE 69101564 D	11-05-1994
			DE 69101564 T	21-07-1994
			JP 4339894 A	26-11-1992
			KR 151592 B	01-10-1998
			US 5382698 A	17-01-1995
			US 5433874 A	18-07-1995
			US 5345002 A	06-09-1994
US 5334775	A	02-08-1994	AU 6664394 A	20-12-1994
			CA 2161418 A	08-12-1994
			DE 69416122 D	04-03-1999
			EP 0701577 A	20-03-1996
			WO 9428035 A	08-12-1994
US 3994698	A	30-11-1976	US 3948619 A	06-04-1976
			CA 966309 A	22-04-1975
			DE 2209579 B	26-07-1976
US 4116644	A	26-09-1978	NONE	
CA 2089833	A	21-08-1993	NONE	
GB 2010324	A	27-06-1979	US 4166726 A	04-09-1979
			AU 521424 B	01-04-1982
			AU 4121578 A	08-05-1980
			BE 872543 A	30-03-1979
			BR 7808275 A	14-08-1979
			CA 1114609 A	22-12-1981
			DE 2853543 A	21-06-1979
			FR 2411882 A	13-07-1979
			JP 1403916 C	09-10-1987
			JP 54087706 A	12-07-1979
			JP 62010279 B	05-03-1987
			NL 7812133 A,B,	19-06-1979
			PH 13904 A	27-10-1980
			SE 438687 B	29-04-1985
			SE 7812741 A	17-06-1979
			ZA 7806072 A	31-10-1979

EPO FORM P459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

